

GW quasiparticle band gaps of anatase TiO_2 starting from DFT+U

Christopher E. Patrick and Feliciano Giustino

Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH,
United Kingdom

E-mail: feliciano.giustino@materials.ox.ac.uk

Abstract. We investigate the quasiparticle band structure of anatase TiO_2 , a wide gap semiconductor widely employed in photovoltaics and photocatalysis. We obtain *GW* quasiparticle energies starting from density-functional theory (DFT) calculations including Hubbard U corrections. Using a simple iterative procedure we determine the value of the Hubbard parameter yielding a vanishing quasiparticle correction to the fundamental band gap of anatase TiO_2 . The band gap (3.3 eV) calculated using this optimal Hubbard parameter is smaller than the value obtained by applying many-body perturbation theory to standard DFT eigenstates and eigenvalues (3.7 eV). We extend our analysis to the rutile polymorph of TiO_2 and reach similar conclusions. Our work highlights the role of the starting non-interacting Hamiltonian in the calculation of *GW* quasiparticle energies in TiO_2 , and suggests an optimal Hubbard parameter for future calculations.

PACS numbers: 71.15.Qe, 71.27.+a, 88.40.H-

The wide gap semiconductor TiO₂ is the subject of a vast research effort owing to its importance to many areas of technology, ranging from photovoltaics and photocatalysis to sensing devices, protective coatings and batteries [1]. As an example, nanostructured anatase TiO₂ films sensitized with molecular dyes are the fundamental building blocks of dye-sensitized solar cells [2]. In order to understand and optimize the photovoltaic and photocatalytic properties of TiO₂ it is important to complement experimental spectroscopies with reliable calculations of electronic excitations in this material and its interfaces.

Band structures calculated within standard DFT underestimate the fundamental band gap of anatase TiO₂ by about 1 eV. The underestimation of the band gap is accompanied by errors of similar magnitude in the individual addition and removal energies, and raises concerns about the calculation of energy-level alignments and charge injection dynamics at interfaces involving TiO₂ [3].

In this context accurate quasiparticle methods for studying electronic excitations, such as the *GW* approximation in its various implementations [4, 5, 6, 7, 8], still face two limitations. (i) On the one hand these methods are computationally demanding, and cannot be used yet for complex systems such as defects and interfaces. For example the minimal atomistic models required to describe donor/acceptor interfaces for solar cells involve several hundreds of atoms [9, 10, 11], which are beyond the reach of current *GW* implementations. (ii) On the other hand, there is the issue of whether *GW* calculations should be performed at the G_0W_0 level, or include some form of self-consistency [8, 12] or off-diagonal matrix elements of the self-energy [12].

In this work we attempt to address the latter point by combining DFT+*U* and G_0W_0 calculations, in the spirit of Kioupakis *et al* [13]. The rationale for this approach is that the use of DFT+*U* as the noninteracting Hamiltonian should provide a better starting point for perturbation theory, thereby legitimizing the use of the G_0W_0 approximation. The Hubbard parameter is determined in such a way that a G_0W_0 calculation starting from the DFT+*U* band structure yields a vanishing correction to the fundamental band gap. This is achieved through an iterative procedure consisting of a sequence of G_0W_0 and DFT+*U* calculations, and can be seen as a simple and inexpensive way to mimic self-consistent *GW*. Using this procedure we obtain a band gap of 3.3 eV for anatase TiO₂. When comparing the band structures obtained from DFT+*U* with or without quasiparticle corrections, we find that they are in reasonable agreement only near the band edges, and that the individual shifts of the bands determined from DFT+*U* are always larger than the corresponding quasiparticle shifts. Interestingly we find that the optimal value of *U* thus determined is transferable to the rutile polymorph of TiO₂.

We perform DFT calculations using the generalized gradient approximation of Perdew *et al* [14] and norm-conserving pseudopotentials [15]. We explicitly include the 3*s* and 3*p* semicore states of Ti in our calculations. The electronic wavefunctions are expanded in a plane waves basis set with a kinetic energy cutoff of 200 Ry, and the Brillouin zone of TiO₂ is sampled using a 6×6×6 Monkhorst-Pack mesh. All DFT calculations are performed using the Quantum ESPRESSO software package [16]. For

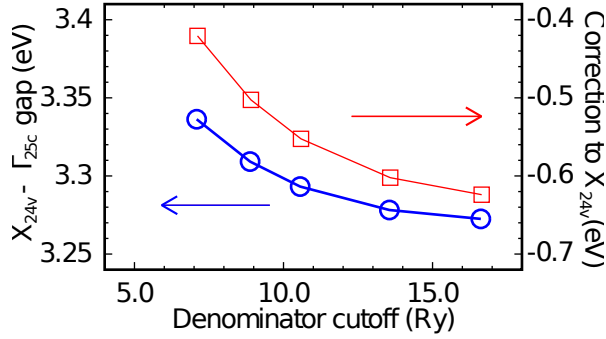


Figure 1. Convergence of GWU calculations with the energy denominator cutoff in the sum-over-states expansions of the polarizability and the Green's function of anatase TiO_2 : $X_{24v} - \Gamma_{25c}$ gap (circles, left scale), and quasiparticle correction to the X_{24v} state (squares, right scale). The quasiparticle corrections were obtained by starting from a DFT+ U calculation with $U=7.5$ eV. The lines are guides to the eye.

definiteness we set the lattice parameters and atomic positions within the unit cell to the experimental values \ddagger [17]. In order to perform DFT+ U calculations [18] we adopt the simplified rotationally invariant formulation of Cococcioni and de Gironcoli [19], with the Hubbard-like corrections included using the atomic Ti $3d$ pseudo-wavefunctions for the projectors. It is worth stressing that, as in every DFT+ U calculation, the value of U determined in this work is linked to the particular choice of the projectors [20]. Quasiparticle GW calculations are performed using the scheme of Hybertsen and Louie [5]. The frequency dependence of the screened Coulomb interaction is described using the Godby-Needs plasmon-pole model [21], by evaluating the static polarizability as well as the polarizability at the imaginary frequency of 23 eV. For the screened Coulomb interaction we use a uniform and unshifted $4 \times 4 \times 4$ Brillouin zone mesh. The exchange and the correlation components of the self-energy are described using plane waves basis sets with kinetic energy cutoffs of 80 Ry and 10 Ry, respectively. In the expansion over conduction states we include 568 unoccupied bands for calculating both the polarizability and the Green's function. The energy denominator cutoff, i.e. the energy of the topmost band used in this expansion referred to the valence band maximum, is 16.6 Ry. Figure 1 shows the convergence of the fundamental gap with the denominator cutoff. Increasing the denominator cutoff from 10.6 Ry (296 conduction bands) to 16.6 Ry (568 bands) reduces the band gap by 0.02 eV. The individual corrections to the band edges converge more slowly, as shown in Figure 1 for the highest occupied state at the X point. All the GW calculations are performed using the **SaX** code [22].

The calculation of GW quasiparticle energies using DFT+ U as the starting non-interacting Hamiltonian is performed as follows. We calculate the G_0W_0 self-energy $\hat{\Sigma}$ using eigenstates and eigenvalues obtained from a DFT+ U calculation. Then, for each Kohn-Sham state ψ of energy ϵ , the quasiparticle energy E is obtained from:

$$E = \epsilon + Z(\epsilon) \langle \psi | \hat{\Sigma}(\epsilon) - V_{xc} - \hat{V}_U | \psi \rangle, \quad (1)$$

\ddagger Our optimized lattice parameters are $a=3.83$ Å and $c=9.84$ Å and the internal parameter is $u=0.206$

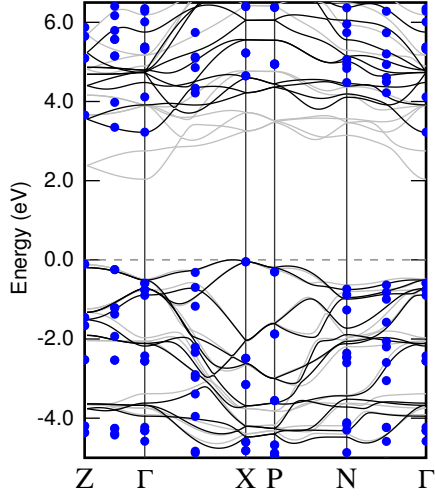


Figure 2. Band structure of anatase TiO_2 calculated using various methods. The gray lines represent standard DFT calculations [14], the black lines are obtained from DFT+ U calculations [19] using our optimal Hubbard parameter $U=7.5$ eV, and the blue disks are from GW calculations using DFT+ U as the non-interacting Hamiltonian. In each case the top of the valence band is arbitrarily aligned with the zero of the energy axis.

where Z is the quasiparticle renormalization, V_{xc} is the DFT exchange and correlation potential, and \hat{V}_U is the Hubbard term in the Kohn-Sham Hamiltonian. The Hubbard contribution to the quasiparticle shift is conveniently evaluated as:

$$\langle \psi | \hat{V}_U | \psi \rangle = \epsilon - \langle \psi | \hat{H}_0 | \psi \rangle, \quad (2)$$

where \hat{H}_0 is the Kohn-Sham Hamiltonian without the Hubbard term (but with the DFT+ U density). In the following we will refer to this procedure simply as GWU method. We have compared the present approach with the method described by Jiang *et al* [23], where the dynamical contributions are evaluated at the energy $\epsilon - \langle \psi | \hat{V}_U | \psi \rangle$, and found the differences to be negligible. In the case of $U=0$ equation (1) yields the standard GW quasiparticle energies obtained by using perturbation theory on top of DFT.

The use of DFT+ U as the starting Hamiltonian for the perturbation expansion introduces an additional arbitrariness in the procedure, relating to the choice of the Hubbard parameter U . Since we are using GW within the framework of perturbation theory, the natural choice for the starting Hamiltonian (and hence the value of U) is the one leading to the smallest quasiparticle corrections. This observation can be formalized into a criterion for choosing the Hubbard parameter: our optimal U is determined by the condition that, upon performing a GWU calculation, the fundamental band gap does not change. This approach has been demonstrated for the case of bcc hydrogen [13]. The optimal Hubbard parameter is determined by using an iterative procedure consisting of successive GWU and DFT+ U calculations, until self-consistency is achieved.

Figure 2 shows that the band gap of anatase TiO_2 is indirect, with the top of the valence band located near the X point of the Brillouin zone, and the bottom of the

conduction band at the Γ point. Since the top of the valence band lies very close in energy with the states at the X point (<60 meV), for convenience in our analysis we take the states at the X point as representative of the valence band top. We denote the band extrema as X_{24v} and Γ_{25c} , respectively [24]. The values of the X_{24v} - Γ_{25c} gap calculated within DFT+U for a range of values of U between 0 and 10 eV are shown in Fig. 3, and are in good agreement with previous work [25]. For $U=0$ we recover the standard DFT band gap of 2.08 eV (indicated by A in figure 3).

Now we go through the iterative calculation of the band gap. We calculate the GW quasiparticle corrections starting from the DFT eigenstates and eigenvalues (i.e. from point A in figure 3), and obtain a corrected band gap of 3.70 eV (point B in figure 3). The latter value is in good agreement with previously published works using the same methodology, 3.6–3.8 eV [24, 26, 27, 28]. We note that the Godby-Needs plasmon-pole model [21] used in our calculations produces a band gap in good agreement (only 0.08 eV larger) with calculations based on the contour deformation method [26], and does not suffer from the overestimation of the band gap reported for other plasmon-pole models [26]. The success of the Godby-Needs approach in reproducing contour deformation results has recently also been demonstrated for ZnO [30]. From figure 3 we see that the same band gap as in B can be obtained by using DFT+U and the Hubbard parameter $U=9.5$ eV (point C). By repeating the previous procedure and applying GW corrections to the DFT+U eigenstates and eigenvalues obtained with $U=9.5$ eV, we find that the quasiparticle corrections slightly reduce the band gap to 3.20 eV (point D in figure 3). We iterate this procedure until the quasiparticle correction to the band gap becomes negligible. The iterations generate the converging series of Hubbard parameters $0.0 \rightarrow 9.5 \rightarrow 7.0 \rightarrow 7.5$ eV, and the series of band gaps $2.08 \rightarrow 3.70 \rightarrow 3.20 \rightarrow 3.29 \rightarrow 3.27$ eV. By the fourth iteration the DFT+U and GWU band gaps are both 3.27 eV and the Hubbard parameter is $U=7.5$ eV. This value of the Hubbard parameter is compatible with the range of values 2-8 eV reported in the literature for oxides containing Ti, cf. Nolan *et al* [29] and references therein. It is interesting to check whether the optimal Hubbard parameter $U_{\text{opt}}=7.5$ eV here determined for anatase TiO_2 is transferable, i.e. (i) whether it generates a band structure in agreement with GWU , and (ii) whether it can also be used for other TiO_2 polymorphs.

In order to address the first point we compare in Fig. 2 the band structures calculated using DFT+U and those calculated using the GWU method, both with $U=U_{\text{opt}}$. Near the band extrema the two methods yield similar results, although differences in energy of up to 0.3 eV are observed for several bands. We also estimate that the GWU calculation yields a valence band width which is 0.3 eV larger than the starting DFT+U band structure. These differences are rather small when compared with the broadening of the valence photoemission spectra reported by Li *et al* [31], corresponding to ~ 1 eV. While the band gaps and band width obtained using DFT+U and GWU are in reasonable agreement, table 1 shows that the corrections to the individual eigenvalues differ significantly. In particular, DFT+U consistently yields energies which are ~ 0.6 eV higher than in GWU .

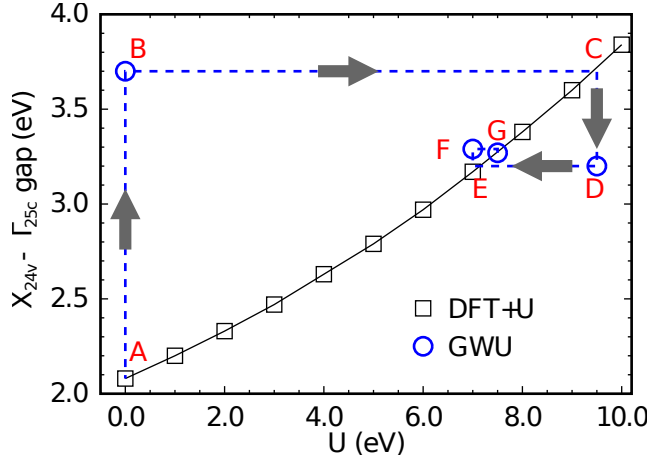


Figure 3. Fundamental band gap ($X_{24v}-\Gamma_{25c}$) of anatase TiO_2 calculated using DFT+U (black squares), and GWU (blue circles), respectively. The lines are guides to the eye.

In order to address the second point we consider the rutile structure. In our DFT and GWU calculations the fundamental gap is direct at the Γ point, therefore in table 1 we only report our results for the Γ_{24v} and Γ_{25c} states. We note, however, that the energies of the conduction band minima of rutile at Γ , M , and R are within 60 meV from each other, and that the location of the minimum is dependent upon the calculation method. Given the small energy difference between direct and indirect gaps in rutile, in order to establish the precise nature of the gap it would be necessary to investigate the magnitude of the phonon-induced renormalization [32, 33, 34, 35]. Table 1 shows that DFT+U and GWU calculations on rutile using U_{opt} lead to very similar band gaps, 2.83 eV and 2.85 eV, respectively. This suggests that the optimal Hubbard parameter U_{opt} determined for anatase is reasonably transferable to rutile TiO_2 . Similarly to the case of anatase TiO_2 , in the rutile polymorph the corrections to the individual eigenvalues calculated in DFT+U are ~ 0.5 eV higher than in GWU .

In the case of anatase TiO_2 we are not aware of published inverse photoemission data on single crystals of anatase, therefore it is not possible yet to perform a quantitative comparison between our calculated quasiparticle energies and experiment. We note however that the measured optical gap of anatase (3.2 eV [37]) is compatible both with our GW band gap (3.75 eV) and our GWU band gap (3.27 eV). In the case of rutile TiO_2 the quasiparticle band gap has been measured in the range 3.3 ± 0.5 eV [38]. This indicates that our GW result (3.40 eV) and our GWU calculation starting from DFT+U (2.85 eV) are both compatible with experiment. The measured optical gap of rutile (3.0 eV [37]) is slightly larger than our calculated quasiparticle gap.

A key result of the present work is that, in the case of anatase and rutile TiO_2 , the use of DFT+U as a starting Hamiltonian for calculating GW quasiparticle energies leads to band gaps which are 0.4 eV smaller than standard GW calculations starting from DFT ([24, 26] and table 1). This relatively large difference between GW and

Table 1. Energies of critical points of anatase and rutile TiO₂ calculated using various methods: plain density-functional calculations (DFT), calculations including Hubbard-like corrections with $U=7.5$ eV (DFT+ U), and G_0W_0 calculations starting from the DFT+ U eigenstates and eigenvalues (GWU). For the sake of comparison with other studies [24, 26, 27, 28] we also report our results for G_0W_0 calculations starting from DFT eigenstates and eigenvalues (GW). All values are in eV. The atomic positions and lattice parameters are taken from experiment [36]. In the case of anatase we also give the values calculated using our optimized lattice parameters between brackets. The choice of theoretical vs. experimental parameters lead to differences smaller than 0.1 eV.

Anatase TiO ₂								
	DFT		GW		DFT+ U		GWU	
X_{24v}	0.00	(0.00)	-0.31	(-0.30)	0.48	(0.49)	-0.14	(-0.13)
Γ_{25c}	2.08	(2.06)	3.39	(3.38)	3.75	(3.70)	3.13	(3.07)
E_g	2.08	(2.06)	3.70	(3.68)	3.27	(3.21)	3.27	(3.20)

Rutile TiO ₂				
	DFT	GW	DFT+ U	GWU
Γ_{24v}	0.00	-0.19	0.59	0.08
Γ_{25c}	1.82	3.21	3.42	2.93
E_g	1.82	3.40	2.83	2.85

GWU raises the question of which Hamiltonian is a better starting point for many-body perturbation theory in strongly correlated systems.

Before concluding we note that, since in the approach described here the optimal Hubbard parameter is determined through an iterative procedure, this scheme carries some similarities with self-consistent GW methods [8]. In the present work the self-consistent potential is constrained to be the DFT exchange and correlation potential plus an additional Hubbard-like term. It would be interesting to apply the same concept to the case of GW calculations starting from hybrid functional calculations [14, 39], where instead of the Hubbard U we would optimize the fraction α of Hartree-Fock exchange.

In conclusion, we investigate the use of DFT+ U as a starting point for performing many-body perturbation theory calculations on TiO₂. We determine the Hubbard parameter of the non-interacting Hamiltonian in such a way that a GW calculation starting from the DFT+ U band structure leaves the fundamental band gap unchanged. We find that the optimal Hubbard parameter of 7.5 eV yields the same band gap of 3.27 eV in DFT+ U and GWU . This value is considerably smaller than the value of 3.70 eV obtained when applying GW corrections to the DFT band structure. The Hubbard parameter determined for anatase is transferable to the rutile polymorph of TiO₂, and also in this case the calculated band gap is smaller than in standard

GW calculations starting from DFT. The difference between *GW* and *GWU* band gaps reported here calls for detailed photoemission experiments to establish whether DFT+*U* represents a better starting point with respect to DFT for computing the *GW* quasiparticle energies of TiO₂.

Acknowledgments

We acknowledge support from the Engineering and Physical Sciences Research Council and from the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement no. 239578.

References

- [1] Diebold U 2003 *Surf. Sci. Rep.* **48** 53–229
- [2] O'Regan B and Grätzel M 1991 *Nature* **353** 737–740
- [3] Martsinovich N and Troisi A 2011 *Energy Environ. Sci.* **4** 4473–4495
- [4] Hedin L 1965 *Phys. Rev.* **139** A796–A823
- [5] Hybertsen M S and Louie S G 1986 *Phys. Rev. B* **34** 5390–5413
- [6] Onida G, Reining L and Rubio A 2002 *Rev. Mod. Phys.* **74** 601–659
- [7] Rinke P, Qteish A, Neugebauer J, Freysoldt C and Scheffler M 2005 *New J. Phys.* **7** 126
- [8] van Schilfgaarde M, Kotani T and Faleev S 2006 *Phys. Rev. Lett.* **96** 226402
- [9] Patrick C E and Giustino F 2011 *Phys. Rev. B* **84** 085330
- [10] Patrick C E and Giustino F 2011 *Adv. Funct. Mater.* **21** 4663–4667
- [11] De Angelis F, Fantacci S, Mosconi E, Nazeeruddin Md K and Grätzel M 2011 *J. Phys. Chem. C* **115** 8825–8831
- [12] Bruneval F, Vast N and Reining L 2006 *Phys. Rev. B* **74** 045102
- [13] Kioupakis E, Zhang P, Cohen M L and Louie S G 2008 *Phys. Rev. B* **77** 155114
- [14] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865–3868
- [15] Fuchs M and Scheffler M 1999 *Comp. Phys. Comm.* **119** 67–98
- [16] P. Giannozzi *et al* 2009 *J. Phys: Condens. Matter* **21** 395502–395520
- [17] Horn M, Schwerdtfeger C F and Meagher E P 1972 *Z. Kristallogr.* **136** 273–281
- [18] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev. B* **44** 943–954
- [19] Cococcioni M and De Gironcoli S 2005 *Phys. Rev. B* **71** 035105
- [20] Pickett W E, Erwin S C and Ethridge E C 1998 *Phys. Rev. B* **58** 1201–1209
- [21] Godby R W and Needs R J 1989 *Phys. Rev. Lett.* **62** 1169–1172
- [22] Martin-Samos L and Bussi G 2009 *Comp. Phys. Comm.* **180** 1416–1425
- [23] Jiang H, Gomez-Abal R I, Rinke P and Scheffler M 2010 *Phys. Rev. B* **82** 045108
- [24] Chiodo L, García-Lastra J M, Iacomino A, Ossicini S, Zhao J, Petek H and Rubio A 2010 *Phys. Rev. B* **82** 045207
- [25] Arroyo-de Dompablo M E, Morales-García A and Taravillo M 2011 *J. Chem. Phys.* **135** 054503
- [26] Kang W and Hybertsen M S 2010 *Phys. Rev. B* **82** 085203
- [27] Mowbray D J, Martinez J I, García Lastra J M, Thygesen K S and Jacobsen K W 2009 *J Phys. Chem. C* **113** 12301–12038
- [28] Thulin L and Guerra J 2008 *Phys. Rev. B* **77** 195112
- [29] Nolan M, Elliott S D, Mulley J S, Bennett R A, Basham M and Mulheran P 2008 *Phys. Rev. B* **77** 235424
- [30] Stankovski M, Antonius G, Waroquiers D, Miglio A, Dixit H, Sankaran K, Giantomassi M, Gonze X, Côté M and Rignanese G-M 2011 *Phys. Rev. B* **84** 241201
- [31] Li S-C, Losovyj Y, Paliwal V K and Diebold U 2011 *J. Phys. Chem. C* **115** 10173–10179

- [32] Marini A 2008 *Phys. Rev. Lett.* **101** 106405
- [33] Giustino F, Louie S G and Cohen M L 2010 *Phys. Rev. Lett.* **105** 265501
- [34] Gonze X, Boulanger P and Côté M 2011 *Ann. Phys.* **523** 168
- [35] Cannuccia E and Marini A 2011 *Phys. Rev. Lett.* **107** 255501
- [36] Abrahams S C and Bernstein J L 1971 *J. Chem. Phys.* **55** 3206–3211
- [37] Kavan L, Grätzel M, Gilbert S E, Klemenz C and Scheel H J 1996 *J. Am. Chem. Soc.* **118** 6716–6723
- [38] Tezuka Y, Shin S, Ishii T, Ejima T, Suzuki S and Sato S 1994 *J. Phys. Soc. Jap.* **63** 347–357
- [39] Perdew J P, Ernzerhof M and Burke K 1996 *J. Chem. Phys.* **105** 9982